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Title:	Challenges of Investigating Redox Reactions in Room Temperature Ionic Liquids
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Challenges of Investigating Redox Reactions in Room Temperature Ionic

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Introduction

▶ The goal of this project is to understand the effects of the morphology and chemical properties of ionic liquids (IL) on the heterogeneous electron transfer processes of simple inorganic ions. This project will seek to understand the fundamental chemical and physical phenomena in ionic liquids through electrochemical, and material characterization techniques.

  ▶ Ionic liquids are organic salts that melt below 100 °C

    ▶ RTIL (room temperature ionic liquids) are salts that are liquids at room temperature

  ▶ Key traits IL exhibit:

    ▶ Their physical properties can be tuned by varying the cations and anions

    ▶ Their ability to function as both a solvent and electrolyte

    ▶ Their electrochemical stability in a broad potential range

    ▶ Recyclability

https://www.chemistryworld.com/features/ionic-liquids-revisted/1017383.article

Introduction

- That goal was not easy to reach due to several factors
  - Photochemical effects
  - The role of water absorption
- It is my hope in this talk to show the issues we had and how we overcame them to get the results we have today

https://www.chemistryworld.com/features/ionic-liquids-revisted/1017383.article

Photochemical effect

- Samples were made In MHMIM Cl with various copper concentrations

- I chose to make all the samples at once. Then leave them out in the lab while I worked on each pair of experiments.

- A change in the open circuit potential suggested the partial reduction of Cu(II)/Cu(I).

- I confirmed with tests using a led light over a long period of time.

- Solution: Place aluminum foil around mixing vial and electrochemical cell and reduce the use of light in the laboratory to the necessary minimum.
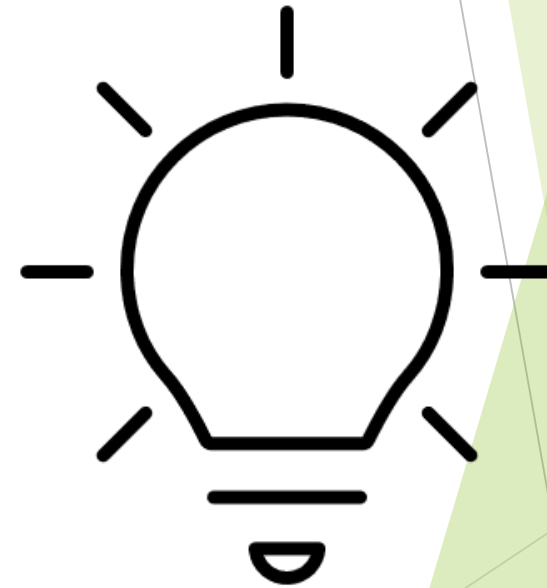
Irreproducibility

▶ Initial study was to test to see if there was a difference electrochemically between hydrated copper chloride and anhydrous copper chloride.

▶ Initial results demonstrated a different electrochemical behavior of hydrated and anhydrous $CuCl_2$ in solution with the same total water content

▶ This prompted time resolved experiments to determine when an equilibrium was reached in each sample.

▶ The observed difference was not seen again after a wait time of 1 hour between each CV scan.

Re-design of experiments

- After the issues we had we redesigned the experiments to get the following results

Experimental Method

Loop (Cycle)
- Chronoamperometry
- Cyclic Voltammetry
- Delay
- Chronoamperometry
- Cyclic Voltammetry
- Delay
- Chronoamperometry
- Cyclic Voltammetry
- Delay
- Chronoamperometry
- Cyclic Voltammetry
- Delay
- Chronoamperometry
- Chronopotentiometry
- Delay
- Chronoamperometry
- Cyclic Voltammetry
- Delay
- Chronoamperometry
- Cyclic Voltammetry
- Delay
- Chronoamperometry
- Cyclic Voltammetry
- Delay
- Potentiostatic EIS
- Delay

Visual of the Gamry experimental script

- Chronoamperometry
- CV
- Delay
- Repeat tests at different scan rates (mV s^{-1})
  - 20, 50, 100, 500, 750, 20 (wider potential window), 20
- Delay
- Impedance

The script is used to ensure that all experiments are performed in an identical way

- **Chronoamperometry**
  - Technique in which the potential of the working electrode is stepped from usually open circuit voltage to the desired voltage and the resulting current monitored as a function of time
    - 10 minutes at 1V
    - To oxidize any Cu(I) present in the vicinity of the electrode surface . The Cu(1) presence is due to the photochemical affect. As well as restoring the equilibrium at the electrode solution interface.
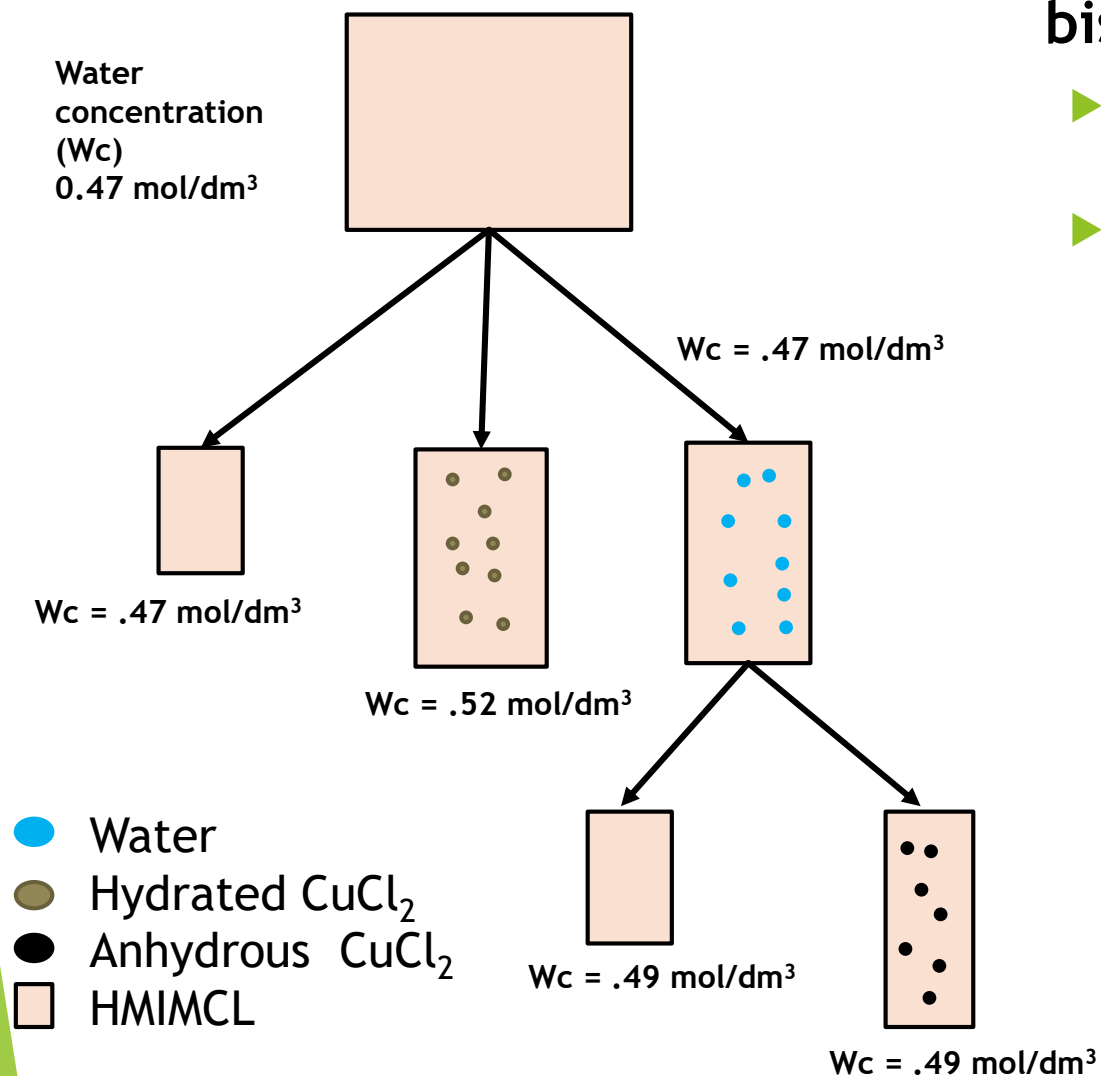   - Not used as a data collection technique

- **Cyclic Voltammetry (CV)**
  - Technique in which the potential of a working electrode is cycled at a desired scan rate (mV/s) as the resulting current is measured
    - Scan range starts at 1V goes to 0V then back to 1V for all scans

- **Electrochemical Impedance Spectroscopy (EIS)**
  - Technique where a small amplitude sinusoidal voltage is applied to an electrochemical cell – allows to determine the resistive and capacitive characteristics of the cell and match them to specific parts of and processes in the cell
    - Used to get the internal resistance of the electrolyte subsequently utilized in simulations of the reactions occurring in the cell
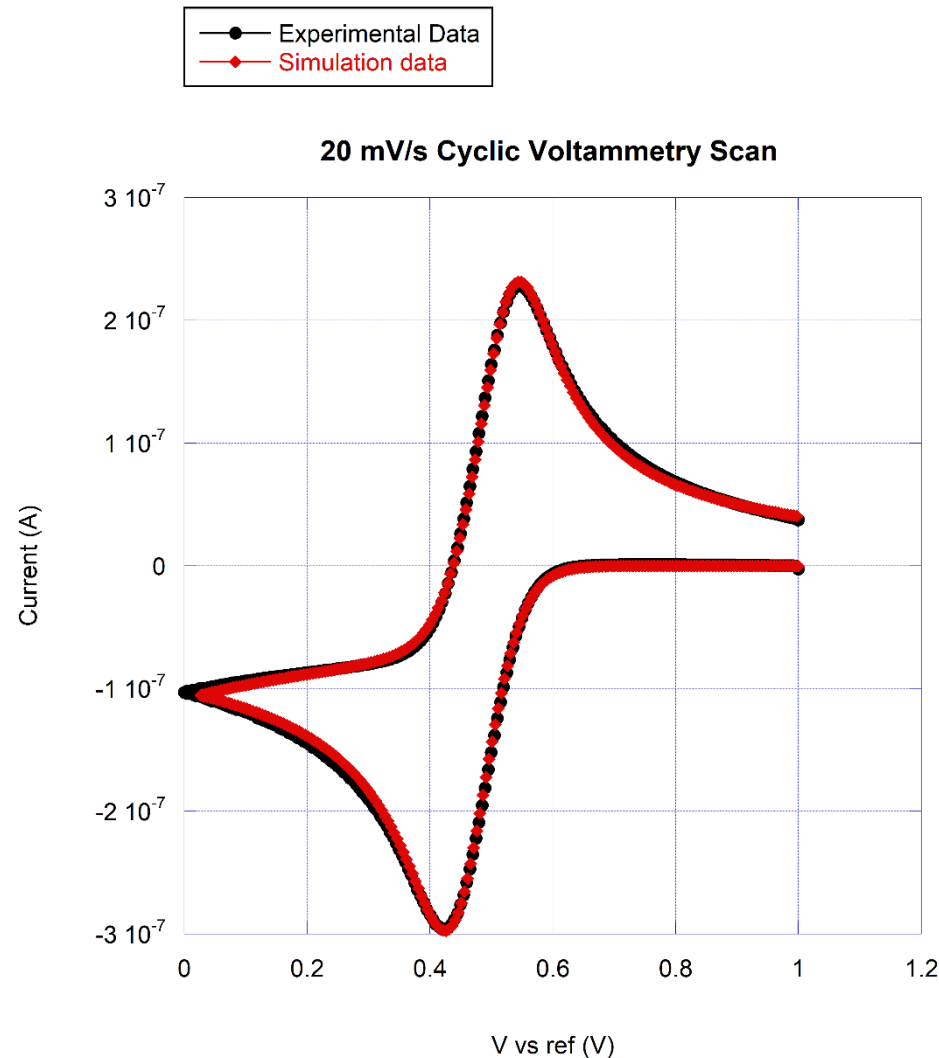
Sample Preparation

Water concentration (Wc) 0.47 mol/dm³

Wc = .47 mol/dm³

Wc = .47 mol/dm³

Wc = .52 mol/dm³

Wc = .49 mol/dm³

Wc = .49 mol/dm³

● Water
● Hydrated $CuCl_2$
● Anhydrous $CuCl_2$
☐ HMIMCL

▶ **1-Hexyl-3-methylimidazolium bis(trifluormethylsulfonyl)chloride (HMIMCl)**

  ▶ Determine water content of HMIMCl through Karl Fisher (KF) titration

  ▶ Separate into three fractions to prepare samples containing identical water content

    ▶ First fraction is designated for background current determination in voltammetry

    ▶ Second fraction - Hydrated copper chloride ($CuCl_2.2H_2O$) is added to the second fraction to produce 0.025 mol/dm³ Cu(II) solution. The total water content is determined by adding the respective numbers from the KF titration and the amount of $CuCl_2.2H_2O$ added

    ▶ Third fraction – Water is added to the third fraction to match the total water concentration in the second fraction after the $CuCl_2.2H_2O$ is added . Then it is split into two portions.

      ▶ First portion is designated for background current determination in voltammetry.

      ▶ Second portion – Anhydrous copper chloride ($CuCl_2$) is added to the second portion to obtain a 0.025 mol/dm³ Cu(II) concentration.

The goal of this preparation process is to have the same water content in all samples

Electrochemical Studies results

Experimental And Simulated Data Of CuCl$_2$ In HMIM Cl

20 mV/s Cyclic Voltammetry Scan

Legend:
- Experimental Data
- Simulation data

Axes: Current (A) vs V vs ref (V)

Example of Data Processing

Experimental parameters
Copper Concentration: 0.0247 mol/dm^3
H$_2$O Concentration: ~ 2 mol/dm^3

Examples of simulation results
Ir (Internal resistance) : 7889 Ω
E* (Standard potential) : 0.48844 V
α (Charge transfer coefficient): 0.47146
k$_s$ (Rate constant) : 3.59E-05 cm/s
Cu^{2+}/Cu$^+$ diffusion coefficients : 2.13E-009 cm^2/s

The equality of diffusion coefficients was an assumption and therefore the k$_s$ corresponds to the reversible half wave potential.

The simulation slightly deviates from the experimental data. That deviation remains within acceptable errors.
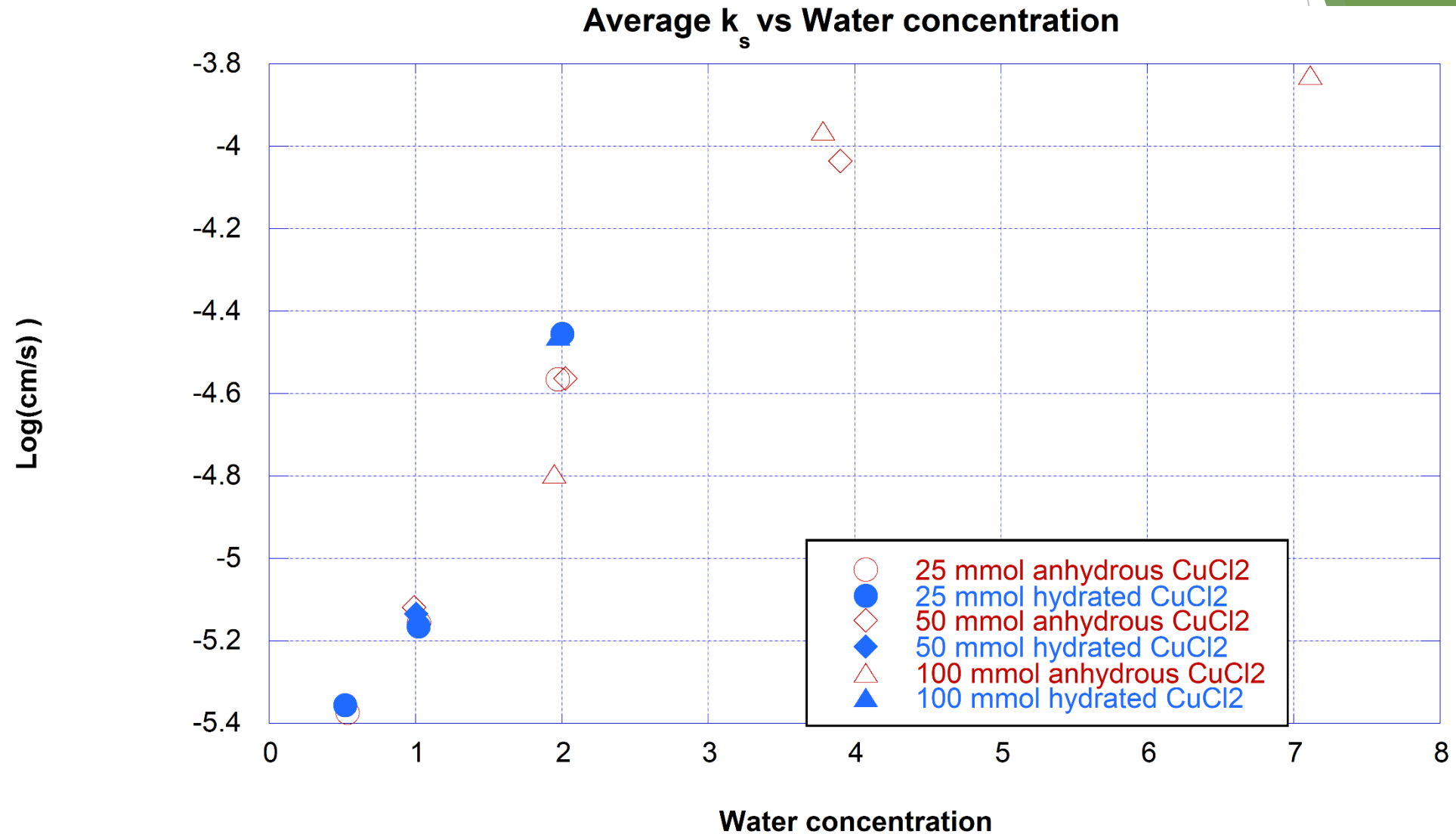
Electrochemical Studies results

Scan Rate	Ir Ω	E*(v)	α/λ	ks	Cu2+	Cu+
20	7889	0.48844	0.47146	3.59E-05	2.13E-09	2.13E-09
50	7889	0.48628	0.46539	3.10E-05	1.90E-09	1.90E-09
100	7889	0.4868	0.47137	2.86E-05	1.90E-09	1.90E-09
200	7889	0.48766	0.45641	2.67E-05	1.90E-09	1.90E-09
500	7889	0.4904	0.44351	2.10E-05	1.75E-09	1.75E-09
750	7889	0.49513	0.39434	2.00E-05	1.75E-09	1.75E-09
20	7889	0.48795	0.47956	2.84E-05	2.13E-09	2.13E-09
Avg		4.89E-01	4.50E-01	2.72E-05	1.89E-09	1.89E-09
std dv		2.99E-03	2.69E-02	5.51E-06	1.27E-10	1.27E-10

Experimental parameters

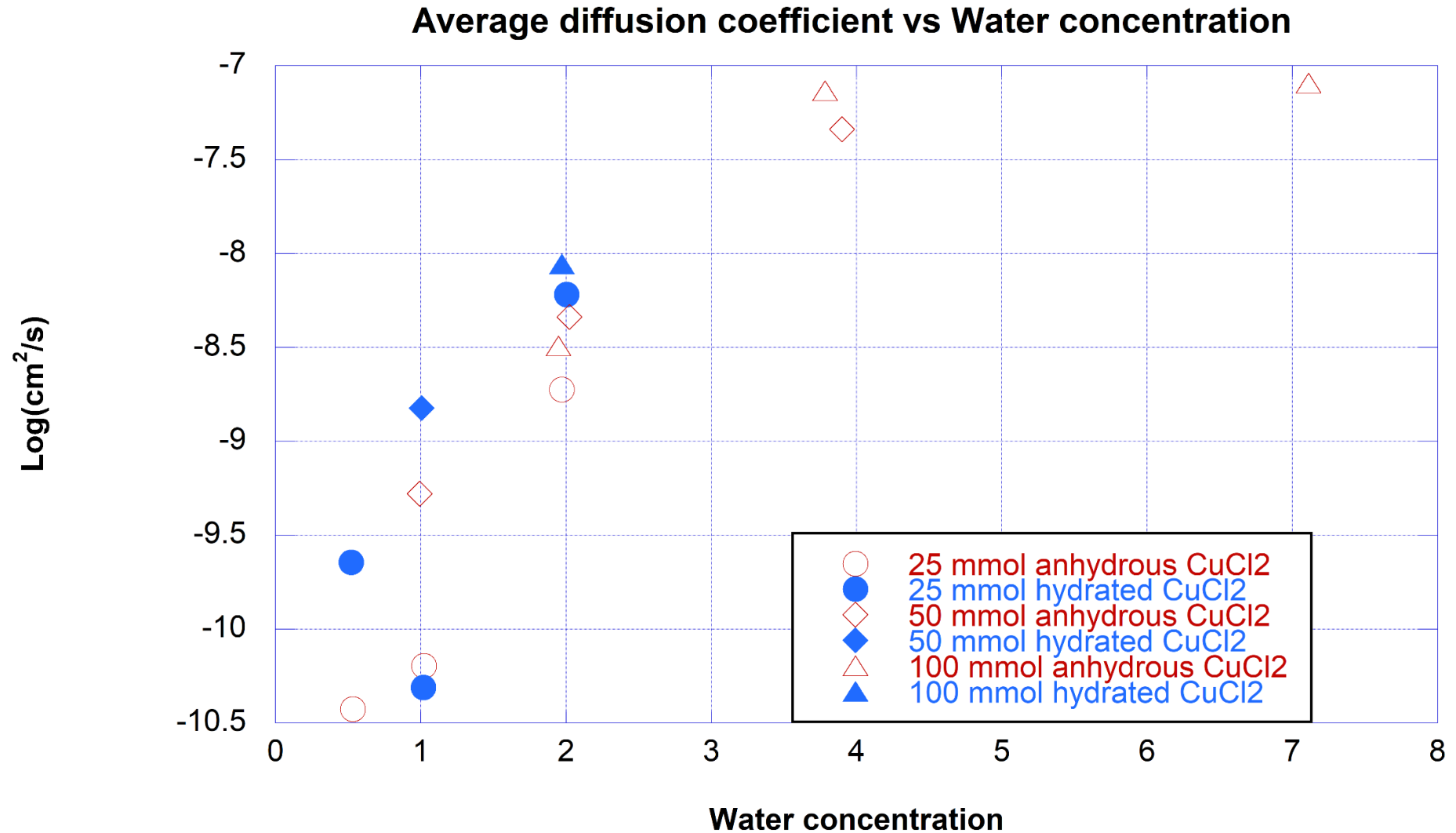Copper Concentration: 0.0247 mol/dm^3 H_2O Concentration: ~ 2 mol/dm^3

Because of simulation errors we are taking the average values for the parameters.

Electrochemical Studies results
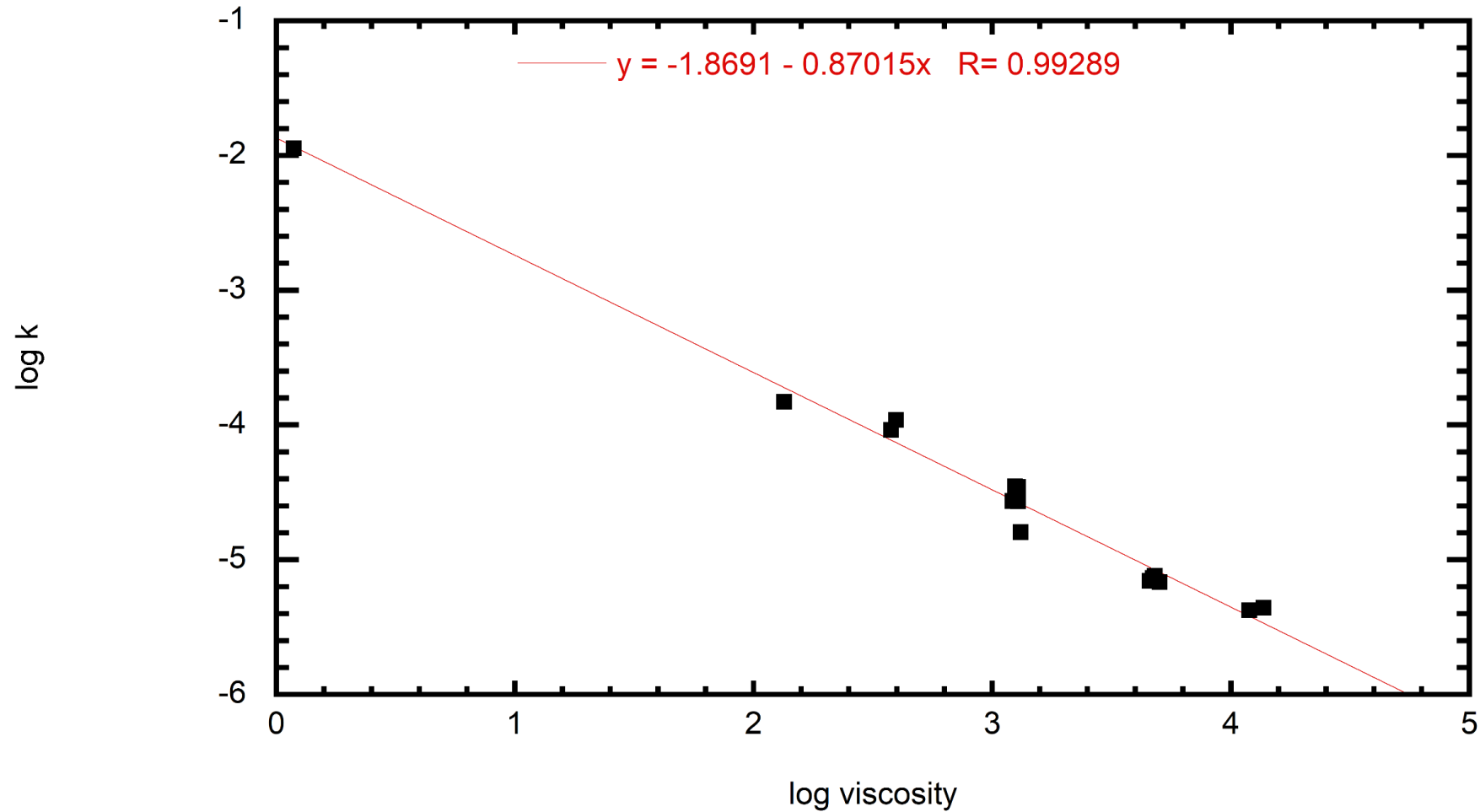

Average k$_s$ vs Water concentration

There is a dependence on the water concentration of the kinetics and diffusion coefficient of Cu^{2+}. This dependence is most likely due to the change in viscosity of the IL.

Electrochemical Studies results

Average diffusion coefficient vs Water concentration

There is a dependence on the water concentration of the kinetics and diffusion coefficient of Cu^{2+}. This dependence is most likely due to the change in viscosity of the IL.

Electrochemical Studies results

There is a dependence on the water concentration of the kinetics and diffusion coefficient of Cu^{2+}. This dependence is most likely due to the change in viscosity of the IL.

Kinetics vs. liquid viscosity

- Linear dependence between $\log(k_s)$ and $\log(\eta)$ with a slope of 0.87, i.e., lower than unity (expected for an adiabatic reaction*)

- Currently considered reasons for the non-unity slope

  - The use of reversible half-wave potentials rather than E^0

  - Complexation equilibria involving water as a ligand

  - Liquid morphology changes

*M. J. Weaver, Chem. Rev. 1992, 92, 463–480

Conclusions

- **In investigating IL/solute solutions sample preparation is important**
  - **Things to consider**
    - **Photochemical effects**
    - **The role of water absorption on the samples**
- **Linear dependence between $\log(k_s)$ and $\log(\eta)$**

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Thank you for your time
Any Questions ?